

ELECTRIC STUDIES ON SOME METAL BIPHTHALOCYANINE COMPLEXES

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ABSTRACT

Metal free biphthalocyanine and some of its metal complexes, namely (Mg, Ca, Sr; Zn, Cd and Sn, Pb) have been prepared by the well known urea fusion technique in the dry and solvent methods.

The behavior of the prepared biphthalocyanine complexes as semiconductors has been investigated and studied within the temperature range which includes their structural phase transition.

The conductivity of the tested samples increases three orders of magnitude on heating from room temperature up to 573 K. Zn and Cd biphthalocyanine complexes show significant change in slope ($\log \sigma$ vs. $1000/T$) at lower temperatures with respect to the tested series of complexes. The activation energies for conduction are calculated in the lower and higher temperature regions. High temperature regions are characterized by higher activation energies.

INTRODUCTION

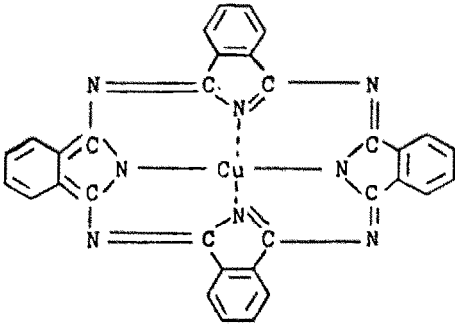
The electrical properties of organic semiconductors have attracted attention in recent years. Phthalocyanines and their derivatives represent the most extensively studied family, probably due to their properties such as thermal stability, semiconductivity, planarity of the molecules and their resemblance to many biologically active materials. The theoretical aspects and literature survey may be found in refs. 1 and 2.

Metal free biphthalocyanine [3] and its metal complexes [4] were prepared and characterized for their use as colored pigments. In a previous study [5] the spectral, magnetic and dielectric properties of some metal biphthalocyanine complexes were investigated. In the present work we intend to throw light on the electrical properties of some metal biphthalocyanine complexes.

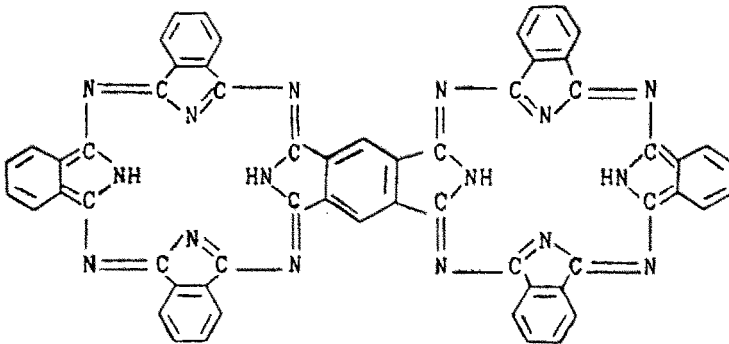
EXPERIMENTAL

Sample preparation

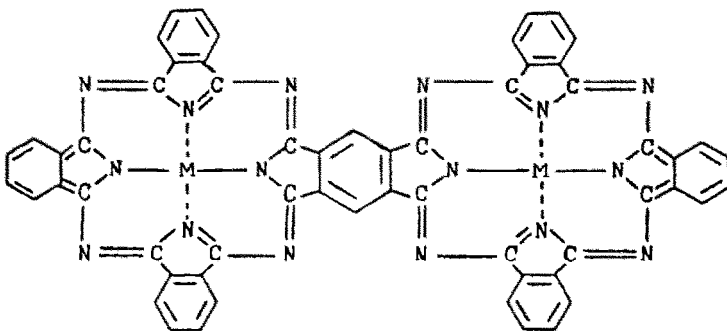
Copper phthalocyanine (I), metal free biphthalocyanine (II) and its metal complexes (III) [3–5] were prepared by urea fusion techniques using dry and



(I) Cu phthalocyanine



(II) Metal free biphthalocyanine



(III) Metal biphthalocyanine complexes (M = Cu, Mg, Ca, Sr, Sn, Pb, Zn and Cd)

solvent methods. Purification of the crude solids was carried out using boiled distilled water, 2% HCl solution, 1% NaOH solution, distilled water, ethanol and finally acetone and drying at 105 °C for 3 h. The samples were subjected to further purification by sublimation under vacuum.

Electrical conductivity measurements

The samples used in this work were of fine powder compressed to pellet form; the pellets were of diameter 12 mm and thickness 2 mm. The pressure used for compression was 5 ton cm⁻². The d.c. conductivities of the samples were measured under a constant d.c. voltage using a two electrode cell. Details of the measuring circuit have previously been published [6].

RESULTS AND DISCUSSION

The semiconducting properties of phthalocyanines were first observed by Eley [6] and by Vartanyan [7]. Eley et al. [8] proposed that the conductivity arose through thermal or optical excitation of electrons from the highest filled to the lowest empty orbital. The mechanism [9] of conductivity is associated with the mobile electrons of the phthalocyanine rings.

Figures 1–3 show the relation between log σ (σ is the conductivity) and the reciprocal of absolute temperature ($1/T$). From these figures it is clear that the behavior obeys the well-known Arrhenius equation

$$\sigma = \sigma_0 e^{-\Delta E/2KT}$$

where σ_0 is a pre-exponential factor, ΔE is the energy gap width and K is the Boltzman constant. The energy gap widths for the different compounds investigated were calculated and are compiled in Table 1 together with values of log σ and the temperature where a break in the straight line occurs. The obtained energy gap widths are lower than those published for metal phthalocyanines [1,2]. The larger molecular structure of the macromolecules is responsible for an increase in conductivity, since additional aromatic rings increase the electron density of the delocalized electrons. The conduction in metal complexes is interpreted in the light of excitation of electrons from the highest filled π bond to the lowest empty π^* bond [8].

From the results obtained, the following observations may be made.

(1) The lower temperature range is characterized by lower activation energy and high resistivities. Such an observation supports the assumption that the conduction in this range is related to the difference between the impurity levels and conduction or valence bond [10].

(2) The higher temperature range is characterized by higher activation energies and lower resistivities. This may be acceptable since it is the intrinsic range of conductivity.

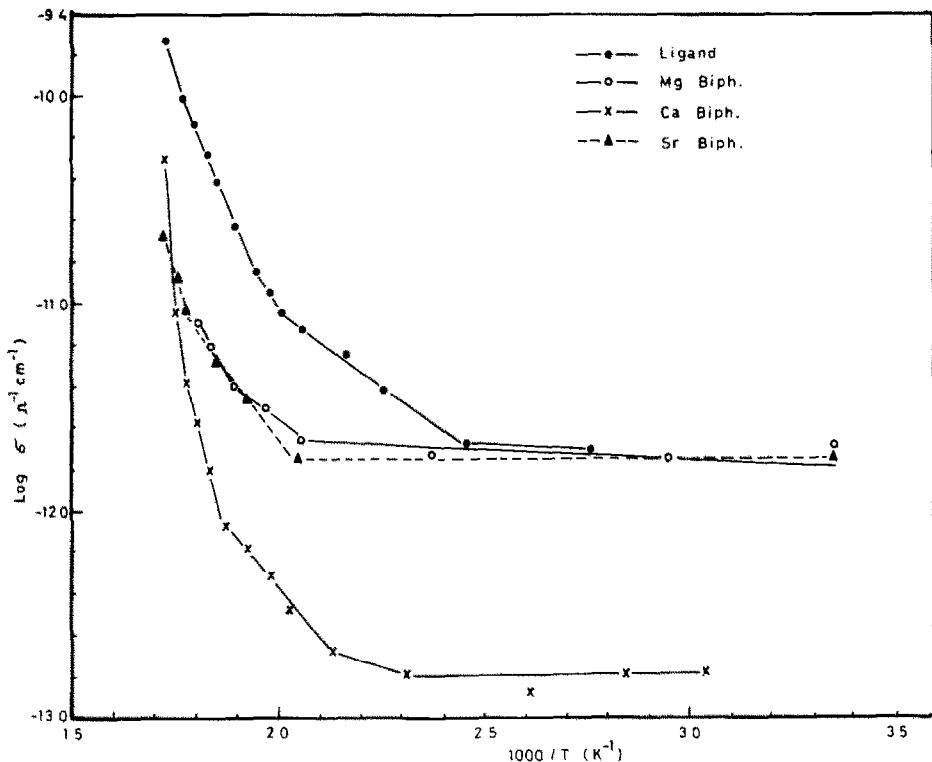


Fig. 1. Variation of log conductivity ($\Omega^{-1} \text{ cm}^{-1}$) with reciprocal absolute temperature (K^{-1}) for Mg, Ca and Sr complexes.

(3) In the case of the Mg, Ca and Sr series, it is expected that bonds between metal and biphthalocyanine will be more covalent, and hence stronger. The results obtained show higher activation energies in both temperature ranges; also the break in slope occurs at relatively higher temperature. The magnesium complex shows lower activation energy and hence higher electron density in the bonding orbitals. It is noteworthy that Mg does not contain vacant d orbitals in the valence shell, and the bonding electrons in the macromolecule are not attracted to the metal atom. The strength of metal–ligand bonds is responsible for the higher break temperature, higher energy gap width and also relatively higher conductivity.

(4) For the other two groups of complexes, similar deductions may be made; that is, with increasing atomic number, the activation energy gets higher. However, the low temperature value for the Pb complex is higher than that of the Sn complex. This contradiction should arise because of the extrinsic nature of conductivity. The break in slope occurs at lower temperature. From the results obtained, some correlations between the electronegativity of the metal and the activation energy of its biphthalocyanine com-

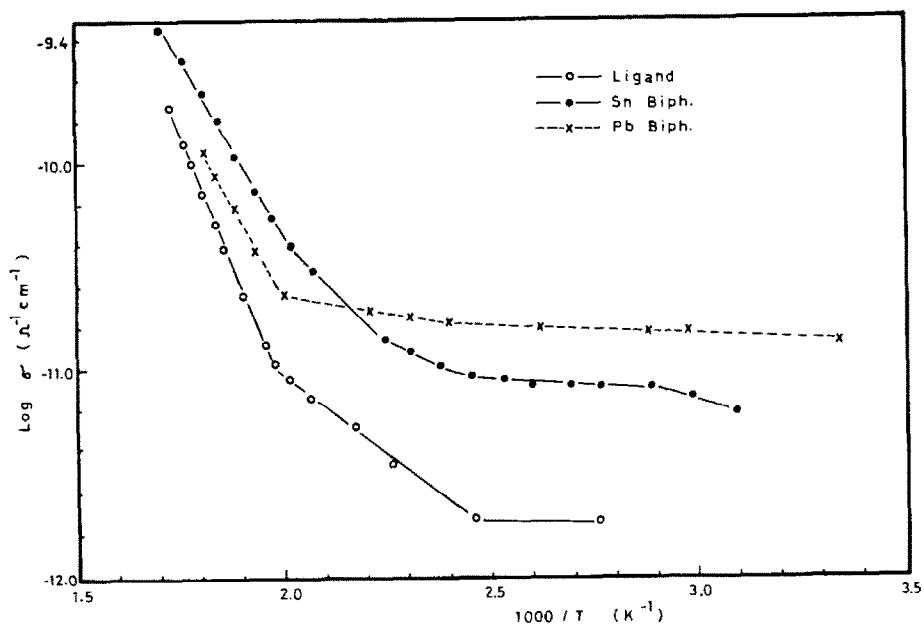


Fig. 2. Variation of log conductivity ($\Omega^{-1} \text{ cm}^{-1}$) with reciprocal absolute temperature (K^{-1}) for Sn and Pb complexes.

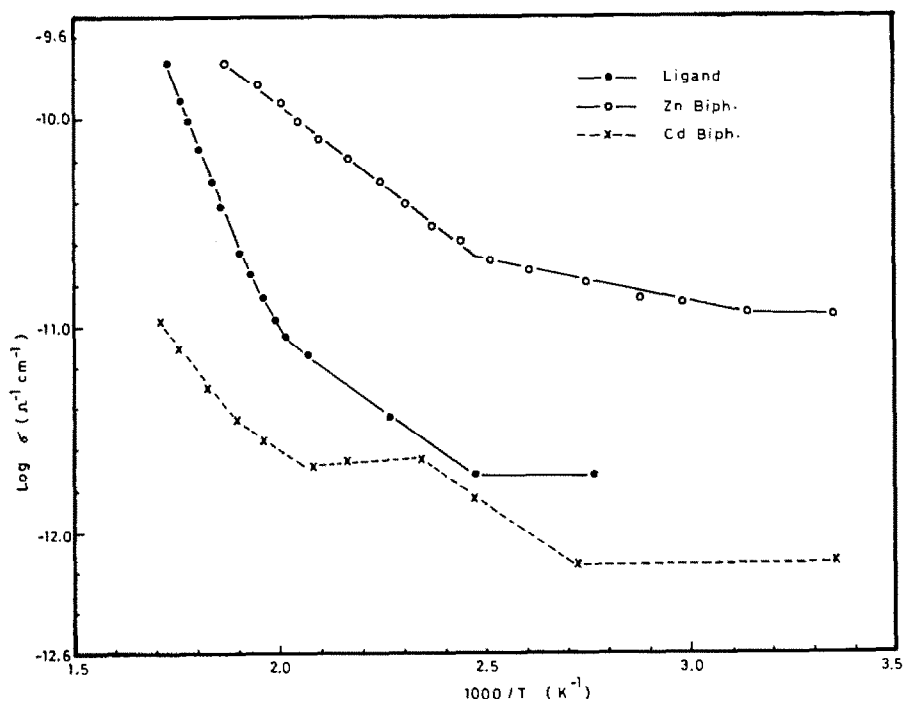


Fig. 3. Variation of log conductivity ($\Omega^{-1} \text{ cm}^{-1}$) with reciprocal absolute temperature (K^{-1}) for Zn and Cd complexes.

TABLE 1
Energy gap width and logarithm of conductivity of investigated biphthalocyanine complexes

Compound	ΔE (eV)		Temp. of change in slope (°C)	log σ	
	Lower temp	Higher temp		Room temp	573 K
Mg	0.60	1.28	256	-11.6	-11.1
Ca	0.93	3.29	260	-12.8	-10.3
Sr	1.05	3.20	286	-11.7	-10.7
Sn	0.80	1.36	225	-11.2	-9.3
Pb	0.14	1.60	221	-10.8	-9.9
Zn	0.148	0.594	140	-10.9	-9.7
Cd	0.55	1.18	150	-12.1	-10.9
Ligand	0.593	1.886	236	-11.75	-9.7

plexes are evident. As the electronegativity increases the activation energy decreases.

The break in the curve should correspond to change in crystalline form. Similar breaks in slopes were observed in metal phthalocyanines and were interpreted as phase transitions from α to β at 180°C [11].

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